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PREPARATION OF HIGHLY UNIFORM LOW DENSITY POLYSTYRENE FOAMS AND THEIR CHARACTERIZATION

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High Internal Phase Emulsion polystyrene foams have been made at Los Alamos National Laboratory for the past decade. As target designs become more complex the demands placed on the foams are more stringent. Parts need to be machined from 30 mg/cm^3 foams to a thickness of 50 μm within a couple of microns. Containing upwards of 97% air, these foams are to withstand extraction with ethanol to remove the wax utilized as a machining aid yet retain their dimensional stability. At low densities, less than 50 mg/cm^3, voids are a problem. To determine a formulation that reduces void content and allows minimum shrinkage, experimental design was utilized. We also developed image analysis techniques that allow us to quantify the amount of voids in the system and the surface finish of the foam. In order to machine these low density foams to the tolerance required with an optimum surface finish, the foams are backfilled with Brij® 78, an alcohol soluble wax. After a part is machined the Brij® is leached out with ethanol. The dimensional stability of the foam was found to be independent of the formulation of the foam. The filler that was used to aid in machining did have a significant impact on the final properties of a machined part.

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Introduction

Foams comprised of only carbon and hydrogen have been the main focus in the Inertial Confinement Fusion targets at Los Alamos National Laboratory for the past five years. Not only has target design become more complex over the years but more demands have been placed on the foams themselves. 50 μm thick parts are made from foams that are three percent full density (that is 97% air!). These parts are expected not to deform or shrink and need to be robust enough to be handled by the assemblers. When a part is a cylinder 250μm in diameter and 75 μm thick, the absence of voids is essential. Recently density gradients within a foam and the presence of voids have also become concerns.[1]

Densities of High Internal Phase Emulsions (HIPE) the foams prepared at LANL range from 30 mg/cm^3 to 650 mg/cm^3 are made by varying the ratio of the oil and water phase. As the density of the foam increases there is a thickening of the struts of the cell along with a closing of the window of the cell wall between adjacent cells. At high densities the foam becomes closed cell. Coalescence of the emulsion leads to the formation of larger cells within the uniform emulsion. These "voids" are one of the two problems addressed in this paper. Voids seem to be more prevalent in low density (< 50 mg/ cm^3) foams. In order to quantify the void content in a foam we first had to settle on a definition for a void since a foam is essentially made up of small voids. For the quantification of voids we define a void as ten times the average pore size.

Experimental design was used to explore the compositional effect on the morphology of the foam. Variables that were evaluated were the percent of surfactant in the oil phase and the crosslink ratio. The purity of monomers, type of surfactant, and initiator type and concentration had been evaluated in an earlier study. The responses that were evaluated were: shrinkage, deformation, void content, and brittleness.

The other issue addressed is the recent appearance of machining artifacts in finished foam parts. In order to machine foam parts with a surface finish on the order of a micron the HIPE foam is backfilled with an alcohol soluble wax, Brij-78®. After the parts are machined the Brij-78® is leached out of the foam with ethanol. When the Brij-78® is leached from the foam the final part shrinks 2% - 5%, depending on the geometry of the part. The ultimate test for a foam is to machine a 50 μm thick washer. Washers prepared from earlier formulations would often curl upon drying.

Experimental

Materials. Styrene, divinylbenzene (DVB), and sodium persulfate were purchased from Aldrich and were used without any further purification. The sorbitan monooleate (SMO) was provided by Lonza, Inc. The Brij® 78 originally used to backfill the foams was purchased from Acros. The Brij® samples used in the evaluation studies of the effects of different waxes on the machining properties of foams were provided by Uniqema.

Instrumentation. Images of foam samples destined for image analysis were acquired using an Olympus BX51 optical microscope equipped with an Optronics Macrofire digital CCD camera. Mercury Intrusion Porosimetry experiments were performed on a Micromeritics Autopore-III.

Preparation of HIPE Foams. An oil phase, consisting of the monomers and surfactant, and an aqueous phase, consisting of water and the initiator, were prepared then mixed using the standard syringe pump technique.[2] For densities higher than 400 mg/cm^3, the emulsion needed to be mixed using a high speed stirrer (~20,000 rpm) in order to get complete incorporation of the oil phase into the water phase. Once the emulsion was formed it was cured at 60°C for 24 hours. The resulting foam was extracted with ethanol to remove the surfactant. The foam was then dried under ambient conditions. The pores formed during the emulsification process are open cell on the order of one to tens of microns in diameter as determined by mercury porosimetry and scanning electron microscopy.

Preparation of Samples for Optical Microscopy. Foam sections were machined on a lathe from cylinders of HIPE foam, approximately 2 mm diameter and 50 μm thick. Image magnification was calibrated using a NIST traceable optical calibration standard. A variety of lighting conditions, imaging modes, and magnifications were used to best visualize the features of interest. For machined surface defects of both Brij filled and dry foams, oblique lighting at a grazing angle was used. For surface voids in dry foam, ambient room lighting favored these features while diminishing the raised surface machining defects. For internal defects in Brij filled foam side lighting created a pseudo dark field that contrasted these features from the Brij extremely well.

Results and Discussion

Experimental Design. To assess the effects of formulation variables on the density and uniformity of the foams, a mixture experiment was devised using statistical design methods. The relative proportions of styrene, DVB, SMO, and water were systematically varied. The design did not include any process variables.

The experimental design was generated with the aid of Design-Expert® software, Stat-Ease, Inc. The objective of the study was to produce a 30 mg/cm^3 foam with uniform porosity, and low shrinkage. The components were bound by the following individual constraints:

$$95.7\% < \text{Water (wt\%)} < 95.85\% \quad (1)$$
$$1.45\% < \text{SMO} < 1.59\% \quad (2)$$
$$1.08\% < \text{DVB} < 1.62 \quad (3)$$
$$1.08\% < \text{Styrene} < 1.62\% \quad (4)$$

and the additive constraints:

$$2.7\% < \text{Styrene} + \text{DVB} < 2.71\% \quad (5)$$
$$97.2\% < \text{SMO} + \text{Water} < 97.3\% \quad (6)$$
$$\text{Styrene} + \text{DVB} + \text{SMO} + \text{Water} = 100\% \quad (7)$$

Sample formulations were then determined for a Mixture Study of D-optimal design with sufficient fidelity to fit a Quadratic model. Automated generation of mixtures, which satisfied all of the above constraints was performed and reduced to a total of 16 mixtures for experimentation. Four components of the formulation were required to be present in the samples since the constraints do not allow values of zero. Two replicates were used to assist in the statistical analysis of fit for the final mixture model.

To determine the relationship between the four mixture components and the resulting foams, statistical analysis was performed on the sample set with respect to each of the shrinkage measurements and the density measurement. It should also be noted that the styrene/DVB boundary ratios in this study are a result of the point selection from the design space. Analysis of shrinkage with respect to the formulation variables yields equivalent results as those seen for the density response. From the mixture experiment on formulation, we have determined that the components themselves do not demonstrate large effects on the final properties of the foam.

Mercury Porosimetry. Pore-size distributions for HIPE foams of different densities are shown in **Figure 1**. As the foam density increases, the average pore-size decreases. Not only does the average pore-size decrease, the amount of polystyrene in the cell walls increases. Both of these factors contribute to a lower volume of mercury intruded into the

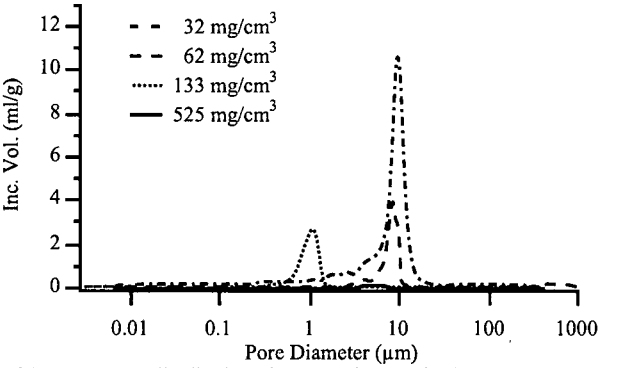

Figure 1. Pore distributions for HIPE foams of different densities.

higher density sample. The amount of mercury that is intruded into the 525 mg/cm^3 sample was due to the closed-cell nature of this foam as observed by SEM.

Density uniformity across a foam monolith can also be tracked by porosimetry and pycnometry. A 50 cm^3 HIPE monolith, with a volumetrically determined density of 62.2 mg/cm^3, was sectioned into 15 pieces, 3 across the block that was sectioned into 5 layers. Average densities of these 15 pieces were found to be 56.62 ± 2.20 mg/cm^3 by pycnometry and 61.22 ± 3.65 mg/cm^3 by porosimetry. Both techniques show density fluctuations under 5% for a sample that is nominally one cm^3.

Stereoscopy. Porosimetry yields data that is quantitative for pore-sizes in ideal systems but there is controversy as to the application of this technique to HIPE foams. An independent quantitative technique that unambiguously measures size distributions of foam cells would be most welcome to help validate the porosimetry. The use of SEMs that is so pervasive in the literature on foams to validate cell size and distributions is unfortunately a common mistake investigators make. SEM imaging (**Figure 2**) is strictly qualitative and not suitable for extracting quantitative cell size distributions and other topometric information such as connectivity and shape or global information such as volume fraction or surface area.

Image analysis using modern stereology techniques can provide the quantitative data necessary to validate the porosimetry results. "Stereology is the science of the geometrical relationships between a structure that exists in three dimensions and the images of that structure that are fundamentally two-dimensional (2D)".[3] Thus image analysis task was to measure the area percent of the voids relative to the total area of the foam in a section. Digital micrographs of a region of the foam require image processing before quantitative analysis can be performed. First the raw image (**Figure 2A**) is calibrated into microns based on a calibration image taken under identical image magnification. A region of interest is then defined (**Figure 2B**). We want to include only the area that is foam and eliminate background and any severely damaged areas that are unsuitable for analysis. Next, the image contrast and brightness was leveled (**Figure 2C**). The final processing step was to threshold the image to clearly discriminate the foam area from the voids. The thresholding was performed manually and based on visual interpretation of color (hue and saturation) and/or intensity histograms depending on the image quality (**Figure 2D**). Four fields from three to five samples were analyzed and a mean and standard deviation was reported for each matrix condition.

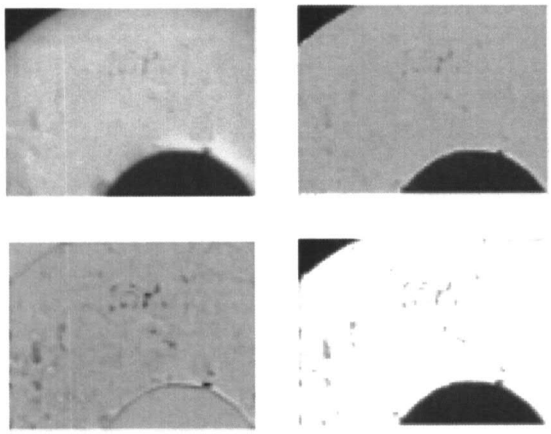

Figure 2. Image processing steps for quantitative image analysis of void volume fraction of a 50 μm thick machined foam disc.

Two types of foam defects were observed using bright field optical microscopy in machined 'washers' of HIPE foams: 1) highly light scattering structures throughout the volume of the Brij® backfilled HIPE foam sample (**Figure 3A**) and 2) irregular, surface roughness after the Brij® backfill was removed (**Figure 3B**). We determined that the internal structures were correlated to the surface features using image processing and analysis tools. Optical micrographs using oblique lighting were taken before and after leaching of the same sample. Translation and rotation of one image relative to the other was required to register the images since between the first and second image, the foam sample had to be moved from its original position for

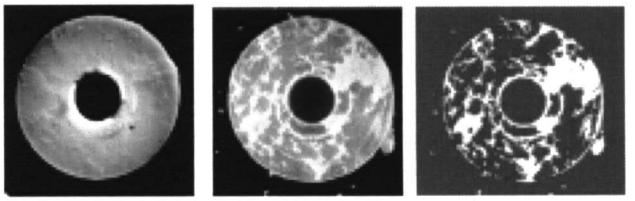

Figure 3. Image processing steps to create composite correlation image. (a) surface defects. (b) internal defects. (c) Binary threshold of internal defects.

leaching out the Brij®. Visual inspection of the resulting composite image proved that the two artifacts were correlated.

It was then determined that the lot of Brij® 78 had an effect on the machining qualities of the final part. Several different lots of Brij® 78 were evaluated along with a lower molecular weight wax, Brij® 76 (m.w. ~ 711 Daltons and 1152 Daltons respectively). Images for the Brij® 76 filled foams did not show any machining artifacts. **Figure 4** shows the surface finishes for three different foams. The machining artifacts can be clearly seen in the washer machined from Brij® 78. Washers machined from Brij® 76 and dry machined do not have these machining artifacts although the surface finish for the washer machined from Brij® 76 is a nominal 2 μm versus a nominal 10 μm for the dry machined washer.

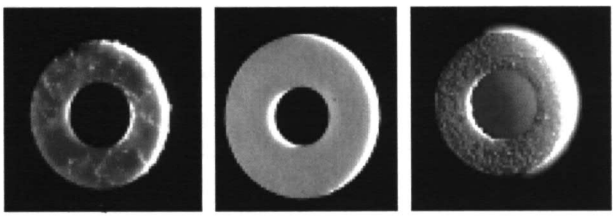

Figure 4. Surface finish for HIPE foams machined: a) from Brij® 78, b) from Brij® 76, and c) dry.

Conclusions

Foams used in the past were held to standards no where near as stringent as today's standards. Not only must the foam have a specific density but they must be uniform. Now by varying the composition of the oil phase we are able to make foams with densities greater than 50 mg/cm^3 without voids. As the density approaches 30 mg/cm^3 voids become more of a problem. With the aid of experimental design we have greatly reduced the amount of voids in the sample. Quantitative image analysis is invaluable in terms of quantifying the quality of the foam. Not only can it be used to determine the percentage of voids in the foam but it was critical in determining the cause of the machining artifacts. Once these correlations were determined we investigated the use of different "waxes" for filling the foams for machining. By switching to Brij® 76 the machining artifacts were no longer observed and the machined parts did not shrink upon leaching.

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References

1. J.M. Williams, "High Internal Phase Emulsion Foams ", *Langmuir* 7, 2298 (1990).
2. G. Magelssen, JOWOG 37 Workshop, Los Alamos National Laboratory, Jan. 2003, private communication.
3. J.C. Russ, R. T. Dehoff, *Practical Stereology*, Ch. 1, Second Edition, Published by Plenum Press, New York, (1999).